

Q-1: Choose the correct answer. A thermodynamic state function is a quantity

- (i) used to determine heat changes
- (ii) whose value is independent of path
- (iii) used to determine pressure volume work
- (iv) whose value depends on temperature only

Ans:

(2) A quantity which is independent of path.

Reason:

Functions like pressure, volume and temperature depends on the state of the system only and not on the path.

Q-2: For the process to occur under adiabatic conditions, the correct condition is:

- (i) $\Delta T = 0$
- (ii) $\Delta p = 0$
- (iii) $q = 0$
- (iv) $w = 0$

Ans:

3: $q = 0$

Reason:

For an adiabatic process heat transfer is zero, i.e. $q = 0$.

Q-3: The enthalpies of all elements in their standard states are:

- (1) Zero
- (2) < 0
- (3) Different for every element
- (4) Unity

Ans:

(1) Zero

Q-4: ΔU

0

of combustion of methane is $-X \text{ kJ mol}^{-1}$. The value of ΔH^\ominus is

(a) $> \Delta U^\ominus$

(b) $= \Delta U^\ominus$

(c) $= 0$

(d) $< \Delta U^\ominus$

Ans:

(d) $< \Delta U^\ominus$

Reason:

$$\Delta H^{\ominus} = \Delta U^{\ominus} + \Delta n_g RT ; \Delta U^{\ominus} = -Y \text{ kJ mol}^{-1},$$

$$\Delta H^{\ominus} = (-Y) + \Delta n_g RT \Rightarrow \Delta H^{\ominus} < \Delta U^{\ominus}$$

Q-5: The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are, $-890.3 \text{ kJ mol}^{-1}$ – $393.5 \text{ kJ mol}^{-1}$, and $-285.8 \text{ kJ mol}^{-1}$ respectively. Enthalpy of formation of $\text{CH}_4 (\text{g})$ will be

(a) $-52.27 \text{ kJ mol}^{-1}$

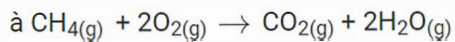
(b) 52 kJ mol^{-1}

(c) $+74.8 \text{ kJ mol}^{-1}$

(d) $-74.8 \text{ kJ mol}^{-1}$

Ans:

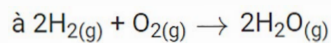
(d) $-74.8 \text{ kJ mol}^{-1}$



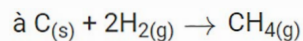
$$\Delta H = -890.3 \text{ kJ mol}^{-1}$$



$$\Delta H = -393.5 \text{ kJ mol}^{-1}$$



$$\Delta H = -285.8 \text{ kJ mol}^{-1}$$



$$\Delta_f H_{\text{CH}_4} = \Delta_c H_c + 2\Delta_f H_{\text{H}_2} - \Delta_f H_{\text{CO}_2}$$

$$= [-393.5 + 2(-285.8) - (-890.3)] \text{ kJ mol}^{-1}$$

$$= -74.8 \text{ kJ mol}^{-1}$$

Q-6: A reaction, $A + B \rightarrow C + D + q$ is found to have a positive entropy change. The reaction will be

- (a) will be possible at low temperature only
- (b) will be possible at high temperature only
- (c) will be possible at any temperature
- (d) won't be possible at any temperature

Ans:

(c) will be possible at any temperature

ΔG should be -ve, for spontaneous reaction to occur

$$\Delta G = \Delta H - T \Delta S$$

As per given in question,

ΔH is -ve (as heat is evolved)

ΔS is +ve

Therefore, ΔG is negative

So, the reaction will be possible at any temperature.

Q-7: In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process?

Ans:

As per Thermodynamics 1st law,

$$\Delta U = q + W(i);$$

ΔU internal energy = heat

W = work done

$W = -594 \text{ J}$ (work done by system)

$q = +801 \text{ J}$ (+ve as heat is absorbed)

Now,

$$\Delta U = 801 + (-594)$$

$$\Delta U = 207 \text{ J}$$

Q-8: The reaction of cyanamide, NH_2CN (s), with dioxygen was carried out in a bomb calorimeter, and ΔU was found to be $-742.7 \text{ kJ mol}^{-1}$ at 298 K. Calculate enthalpy change for the reaction at 298 K.



Ans:

ΔH is given by,

$$\Delta H = \Delta U + \Delta n_g RT \dots\dots\dots(1)$$

Δn_g = change in number of moles

ΔU = change in internal energy

Here,

$$\Delta n_g = \sum n_g(\text{product}) - \sum n_g(\text{reactant})$$

$$= (2 - 2.5) \text{ moles}$$

$$\Delta n_g = -0.5 \text{ moles}$$

Here,

$$T = 298\text{K}$$

$$\Delta U = -753.7 \text{ kJmol}^{-1}$$

$$R = 8.314 \times 10^{-3} \text{ kJmol}^{-1} \text{ K}^{-1}$$

Now, from (1)

$$\Delta H = (-753.7 \text{ kJmol}^{-1}) + (-0.5 \text{ mol})(298 \text{ K})(8.314 \times 10^{-3} \text{ kJmol}^{-1} \text{ K}^{-1})$$

$$= -753.7 - 1.2$$

$$\Delta H = -754.9 \text{ kJmol}^{-1}$$

Q-9: Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g of aluminium from 35°C to 55°C . Molar heat capacity of Al is $24 \text{ J mol}^{-1} \text{ K}^{-1}$.

Ans:

Expression of heat(q),

$$q = mCP\Delta T; \dots\dots\dots(a)$$

ΔT = Change in temperature

c = molar heat capacity

m = mass of substance

From (a)

$$q = \left(\frac{50}{27} \text{ mol}\right)(24 \text{ mol}^{-1} \text{ K}^{-1})(20 \text{ K})$$

$$q = 888.88 \text{ J}$$

Q-10: Calculate the enthalpy change on freezing of 1.0 mol of water at 10.0°C to ice at -10.0°C . $\Delta_{\text{fus}}H = 6.03 \text{ kJ mol}^{-1}$ at 0°C .

$$C_p[H_2O(l)] = 75.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$C_p[H_2O(s)] = 36.8 \text{ J mol}^{-1} \text{ K}^{-1}$$

Ans:

ΔH_{total} = sum of the changes given below:

(a) Energy change that occurs during transformation of 1 mole of water from 10°C to 0°C .

(b) Energy change that occurs during transformation of 1 mole of water at 0°C to 1 mole of ice at 0°C .

(c) Energy change that occurs during transformation of 1 mole of ice from 0°C to $(-10)^{\circ}\text{C}$.

$$\Delta H_{\text{total}} = C_p[H_2O(l)]\Delta T + \Delta H_{\text{freezing}} + C_p[H_2O(s)]\Delta T$$

$$= (75.3 \text{ J mol}^{-1} \text{ K}^{-1})(0 - 10)\text{K} + (-6.03 \times 1000 \text{ J mol}^{-1}) + (36.8 \text{ J mol}^{-1} \text{ K}^{-1})(-10 - 0)\text{K}$$

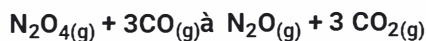
$$= -753 \text{ J mol}^{-1} - 6030 \text{ J mol}^{-1} - 368 \text{ J mol}^{-1}$$

$$= -7151 \text{ J mol}^{-1}$$

$$= -7.151 \text{ kJ mol}^{-1}$$

Thus, the required change in enthalpy for given transformation is $-7.151 \text{ kJ mol}^{-1}$.

Q-11: Enthalpies of formation of CO(g), CO₂ (g), N₂O(g) and N₂O₄ (g) are –110, – 393, 81 and 9.7 kJ mol^{–1} respectively. Find the value of Δ_rH for the reaction:

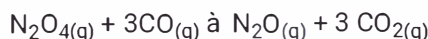


Ans:

“Δ_rH for any reaction is defined as the difference between Δ_fH value of products and Δ_fH value of reactants.”

$$\Delta_r H = \sum \Delta_f H(\text{products}) - \sum \Delta_f H(\text{reactants})$$

Now, for



$$\Delta_r H = [(\Delta_f H(\text{N}_2\text{O}) + (3\Delta_f H(\text{CO}_2)) - (\Delta_f H(\text{N}_2\text{O}_4) + 3\Delta_f H(\text{CO}))]$$

Now, substituting the given values in the above equation, we get:

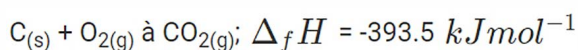
$$\Delta_r H = [81 \text{ kJ mol}^{-1} + 3(-393) \text{ kJ mol}^{-1}] - [9.7 \text{ kJ mol}^{-1} + 3(-110) \text{ kJ mol}^{-1}] \quad \Delta_r H =$$

$$-777.7 \text{ kJ mol}^{-1}$$

Q-12 Enthalpy of combustion of carbon to CO₂ is –393.5 kJ mol^{–1}. Calculate the heat released upon formation of 35.2 g of CO₂ from carbon and dioxygen gas.

Ans:

Formation of carbon dioxide from di-oxygen and carbon gas is given as:



$$1 \text{ mole CO}_2 = 44\text{g}$$

$$\text{Heat released during formation of 44g CO}_2 = -393.5 \text{ kJ mol}^{-1}$$

Therefore, heat released during formation of 37.2g of CO₂ can be calculated as

$$= \frac{-393.5 \text{ kJ mol}^{-1}}{44\text{g}} \times 37.2\text{g}$$

$$= -332.69 \text{ kJ mol}^{-1}$$

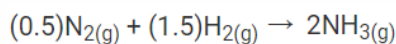
Q-13: Given N₂ (g) + 3H₂ (g) → 2NH₃ (g) ; Δ_rH⁰ = –92.4 kJ mol^{–1}

What is the standard enthalpy of formation of NH₃ gas?

Ans:

“Standard enthalpy of formation of a **compound** is the enthalpy that takes place during the formation of 1 mole of a substance in its standard form, from its constituent elements in their standard state.”

Dividing the chemical equation given in the question by 2, we get



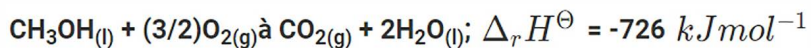
Therefore, Standard Enthalpy for formation of ammonia gas

$$= (0.5) \Delta_r H^\ominus$$

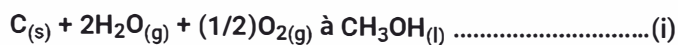
$$= (0.5)(-92.4 \text{ kJ mol}^{-1})$$

$$= -46.2 \text{ kJ mol}^{-1}$$

Q-14: Calculate the standard enthalpy of formation of CH₃OH(l) from the following data:



Ans:



CH₃OH_(l) can be obtained as follows,

$$\Delta_f H_\ominus [\text{CH}_3\text{OH}_{(l)}] = \Delta_c H_\ominus$$

$$2\Delta_f H_\ominus - \Delta_r H_\ominus$$

$$= (-393 \text{ kJ mol}^{-1}) + 2(-286 \text{ kJ mol}^{-1}) - (-726 \text{ kJ mol}^{-1})$$

$$= (-393 - 572 + 726) \text{ kJ mol}^{-1}$$

$$= -239 \text{ kJ mol}^{-1}$$

$$\text{Thus, } \Delta_f H_\ominus [\text{CH}_3\text{OH}_{(l)}] = -239 \text{ kJ mol}^{-1}$$

Q-15: Calculate the enthalpy change for the process

CCl_{4(g)} → C_(g) + 4Cl_(g) and determine the value of bond enthalpy for C-Cl in CCl_{4(g)}.

$$\Delta_{vap} H^\ominus (\text{CCl}_4) = 30.5 \text{ kJ mol}^{-1}.$$

$$\Delta_f H^\ominus (\text{CCl}_4) = -135.5 \text{ kJ mol}^{-1}.$$

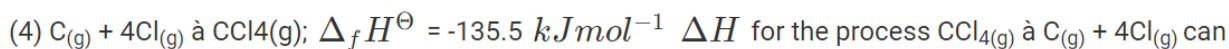
$$\Delta_a H^\ominus (\text{C}) = 715 \text{ kJ mol}^{-1},$$

$\Delta_a H^\ominus$ is a enthalpy of atomisation

$$\Delta_a H^\ominus (\text{Cl}_2) = 242 \text{ kJ mol}^{-1}.$$

Ans:

“ The chemical equations implying to the given values of enthalpies” are:



be measured as:

$$\Delta H = \Delta_a H^\ominus (\text{C}) + 2\Delta_a H^\ominus (\text{Cl}_2) - \Delta_{vap} H^\ominus - \Delta_f H$$

$$= (715 \text{ kJ mol}^{-1}) + 2(242 \text{ kJ mol}^{-1}) - (30.5 \text{ kJ mol}^{-1}) - (-135.5 \text{ kJ mol}^{-1})$$

$$\text{Therefore, } H = 1304 \text{ kJ mol}^{-1}$$

The value of bond enthalpy for C-Cl in $\text{CCl}_{4(g)}$

$$= \frac{1304}{4} \text{ kJ mol}^{-1}$$

$$= 326 \text{ kJ mol}^{-1}$$

Q-16: For an isolated system, $\Delta U = 0$, what will be ΔS ?

Ans:

ΔU is positive ; $\Delta U > 0$.

As, $\Delta U = 0$ then ΔS will be +ve, as a result reaction will be spontaneous.

Q-17:

Following reaction takes place at 298K,



$$\Delta H = 400 \text{ kJmol}^{-1}$$

$$\Delta H = 0.2 \text{ kJmol}^{-1} \text{K}^{-1}$$

Find the temperature at which the reaction become spontaneous considering ΔS and ΔH to be constant over the entire temperature range?

Ans:

Now,

$$\Delta G = \Delta H - T\Delta S$$

Let, the given reaction is at equilibrium, then ΔG will be:

$$T = (\Delta H - \Delta G) \frac{1}{\Delta S} \frac{\Delta H}{\Delta S}; (\Delta G = 0 \text{ at equilibrium})$$

$$= 400 \text{ kJmol}^{-1} / 0.2 \text{ kJmol}^{-1} \text{K}^{-1}$$

Therefore, $T = 2000\text{K}$

Thus, for the spontaneous, ΔG must be -ve and $T > 2000\text{K}$.

Q-18: $2\text{Cl}_{(g)} \rightarrow \text{Cl}_{2(g)}$

In above reaction what can be the sign for ΔS and ΔH ?

Ans:

ΔS and ΔH are having negative sign.

The reaction given in the question represents the formation of Cl molecule from Cl atoms. As the formation of bond takes place in the given reaction. So, energy is released. So, ΔH is negative.

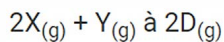
Also, 2 moles of Chlorine atoms is having more randomness than 1 mole of chlorine molecule. So, the spontaneity is decreased. Thus, ΔS is negative.

Q-19: $2X_{(g)} + Y_{(g)} \rightarrow 2D_{(g)}$

$$\Delta U^{\ominus} = -10.5 \text{ kJ and } \Delta S^{\ominus} = -44.1 \text{ JK}^{-1}$$

Determine ΔG^{\ominus} for the given reaction, and predict that whether given reaction can occur spontaneously or not.

Ans:



$$\Delta n_g = 2 - 3$$

$$= -1 \text{ mole}$$

Putting value of ΔU^{\ominus} in expression of ΔH :

$$\Delta H^{\ominus} = \Delta U^{\ominus} + \Delta n_g RT$$

$$= (-10.5 \text{ kJ}) - (-1)(8.314 \times 10^{-3} \text{ kJK}^{-1} \text{ mol}^{-1})(298 \text{ K})$$

$$= -10.5 \text{ kJ} - 2.48 \text{ kJ}$$

$$\Delta H^{\ominus} = -12.98 \text{ kJ}$$

Putting value of ΔS^{\ominus} and ΔH^{\ominus} in expression of ΔG^{\ominus} :

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T \Delta S^{\ominus}$$

$$= -12.98 \text{ kJ} - (298 \text{ K})(-44.1 \text{ JK}^{-1})$$

$$= -12.98 \text{ kJ} + 13.14 \text{ kJ}$$

$$\Delta G^{\ominus} = 0.16 \text{ kJ}$$

As, ΔG^{\ominus} is positive, the reaction won't occur spontaneously.

Q-20: The equilibrium constant for a reaction is 10. What will be the value of ΔG^{\ominus} ? $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$, $T = 300 \text{ K}$.

Ans:

Now,

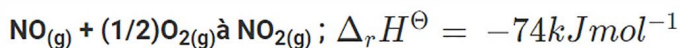
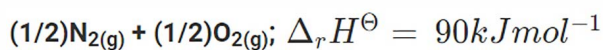
$$\Delta G^{\ominus} = -2.303 RT \log eq$$

$$= (2.303)(8.314 \times 10^{-3} \text{ kJK}^{-1} \text{ mol}^{-1})(300 \text{ K}) \log 10$$

$$= -5744.14 \text{ J mol}^{-1}$$

$$-5.744 \text{ kJ mol}^{-1}$$

Q-21: Comment on the thermodynamic stability of NO(g), given,



Ans:

The +ve value of $\Delta_r H$ represents that during NO_(g) formation from O₂ and N₂, heat is absorbed. The obtained product, NO_(g) is having more energy than reactants. Thus, NO_(g) is unstable.

The -ve value of $\Delta_r H$ represents that during NO_{2(g)} formation from O_{2(g)} and NO_(g), heat is evolved. The obtained product, NO_{2(g)} gets stabilized with minimum energy.

Thus, unstable NO_(g) converts into stable NO_{2(g)}.

Q-22: Calculate the entropy change in surroundings when 1.00 mol of H₂O(l) is formed under standard conditions. $\Delta_f H^\ominus = -286 \text{ kJ mol}^{-1}$.

Ans:

$\Delta_r H^\ominus = -286 \text{ kJ mol}^{-1}$ is given so that amount of heat is evolved during the formation of 1 mole of H₂O(l).

Thus, the same heat will be absorbed by surrounding. $Q_{\text{surr}} = +286 \text{ kJ mol}^{-1}$.

$$\text{Now, } \Delta S_{\text{surr}} = Q_{\text{surr}}/T$$

$$\text{Therefore, } \Delta S_{\text{surr}} = 959.73 \text{ J mol}^{-1} \text{ K}^{-1}$$